

FLOW PROPERTIES OF ASPHALT CEMENTS BY COMPOUNDING WITH SYNTHETIC POLYMERS

Pei-Hung Yeh, Ioan I. Negulescu and William H. Daly
Macromolecular Studies Group, Department of Chemistry,
Louisiana State University, Baton Rouge, LA 70803-1804
Louay N. Mohammad

Department of Civil Engineering and Environmental Engineering,
Louisiana State University, Baton Rouge, LA 70803

INTRODUCTION

Modification of asphalt cements with polymeric materials is widely used to improve pavement performances. Since the addition of polymers increases the cost of the corresponding polymer modified asphalt cement, industrial by-products and recycled polymers have been utilized as the modifiers within the past few years. However, understanding an asphalt-polymer system plays an important role in developing modified asphalts. This includes an understanding of the chemistry and mechanics of compatibility, reinforcement, and stability, and developing of new techniques to characterize modified asphalt binders.

Standard procedures for studying the physical and engineering properties of asphalt have been developed under auspices of the Strategic Highway Research Program (SHRP).¹ Testing and grading systems are based on measuring engineering properties that are related in a more rational way to the pavement performance. The new test methods offer the capability of measuring some properties such as rigidity, elasticity, brittleness, and durability in conditions that simulate loading and climatic conditions encountered in the field.

Our research has been devoted to characterizing asphalts and polymer modified asphalts. Polyethylene (HDPE), a recyclable waste polymer, was slightly chlorinated to improve its compatibility with asphalt.² Both HDPE and chlorinated polyethylene (CPE) modified asphalts were studied according to the Strategic Highway Research Program (SHRP) test methods to quantify the interaction of polymer with the asphalt matrix. The results of a testing protocol based upon thorough rheological evaluation of asphalts both before and after simulated aging, as well as three-point bending data at low temperature to ascertain brittleness will be reported. Preliminary characterization results on asphalt cements prepared with a CPE modified binder will be presented.

MATERIALS AND METHODS

Asphalts and Polymeric Additives

Modified asphalts were prepared using AC-10 grade materials. Polymers investigated as asphalt additives were high density polyethylene (HDPE) and chlorinated polyethylene (CPE). The properties of HDPE and CPE's (5.8 and 24.5 wt% Cl) prepared for this study were determined as previously described.³

The asphalt was heated to 150°C and stirred vigorously while either HDPE or CPE was added. Then the polymer asphalt blend was stirred at 150°C for 40 minutes.

Representative asphalts and modified asphalts were selected for thin film oven test (TFOT) and pressure aging vessel (PAV). All samples (50±0.5g) were aged in the TFOT oven @ 163°C for 5 hours under a continuous air flow. The TFOT samples were submitted to next aging step in the PAV at 100°C and 300 psi for 20 hours.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) data were obtained using a SEIKO DSC 220C instrument with a rate of 10°C/min. Each specimen was cooled from room temperature to -140°C, then heated from -140 to 160°C, and then was cooled from 160 to -100°C at the same rate. The glass transition temperatures (T_g), melting points (T_m), and enthalpy (ΔH) of the blend components were determined as previously described.⁴

Rheology Measurements

A dynamic shear rheometer (Bohlin CVO) was used for dynamic mechanical analysis of asphalt binders with the stress of 150 Pa @ 1.5 Hz. The samples were "sandwiched" between two parallel plates with a diameter of 25 mm at a gap of 1 mm and cooled down to 5°C through one cycle before recording measurements. The reference temperature was taken as $T = 64^{\circ}\text{C}$ to comply with the performance graded asphalt binder specification particularized for the hot climate typical of Louisiana.

Bending Beam Rheometer measurements

The bending beam rheometer (Applied Test System) was used to characterize the low temperature stiffness response of PAV aged tank asphalts and asphalt/polymer blends. The data, which were recorded at six loading times (8, 15, 30, 60, 120, and 240 sec) for a load on the beam of 100 ± 5 g, allowed the calculation of the creep stiffness, $S(t)$, and the creep rate of the sample under load, m , as the absolute value of the slope of the log creep stiffness versus log loading time curve.

Creep and Recovery Tests

A constant stress creep/creep recovery test was run at 50°C with a Haake rheometer (RheoStress RS150) using a 25 mm parallel plate system with a gap of 0.25 mm. During a first test stage, the specimen was subjected to a creep stress of 100 Pa. The resulting deformation were measured and recorded. The resiliency of the asphalt binders was evaluated after the first test phase, then the stress was released and the specimen was allowed to relax to an equilibrium deformation. The elastic recovery can be calculated by the retained deformation caused by the irreversible viscous flow process.

RESULTS AND DISCUSSION

The thermal behavior of asphalt/polymer blend is complex, and depends on asphalt sources and polymer types. Figure 1 is DSC curves of AC-10 blended with HDPE or CPE, which shows that the thermogram of AC10/HDPE blend has the melting peak (T_m) at 120°C . However, in the thermogram of AC10/CPE blend it moved down to 113°C . This phenomenon indicates that introduction of chlorine atoms onto the polymer chain can change the polymer polarity as well as the morphology by reducing the crystallinity. The resultant modification adjusts the interaction parameters to enhance dispersion of both the crystalline and amorphous regions into the asphalt phase. The T_m of CPE compounded with AC-10 decreases dramatically as the chlorine content increases. For instance, it has been observed that T_m of CPE (24.5 %wt Cl) went down to 46°C when blended with AC-10 (Figure 1).

Dynamic shear tests are advantageous because the data can be acquired in a loading mode that is similar to that of traffic loading. All isochronal $\sin\delta$ curves of blends with HDPE as illustrated in Figure 2 approached unity at higher temperatures as the viscoelastic fluids begun to flow. A $\sin\delta$ of unity confirms that the flow is Newtonian and that the polymer particles do not interfere with the measurement. However, as Figure 3 depicts, the $\sin\delta$ of blends with CPE curves are substantially less than one. Clearly, the asphalt binders containing CPE are not Newtonian even at high temperatures. The chlorinated HDPE exhibits good interaction with the polar fractions of asphalt cement which could result in increased visco-elastic properties in AC10/CPE binders and improve the pavement performance.

In Strategic Highway Research Program asphalt specifications, the stiffness parameter, $G^*/\sin\delta$, was selected to express the contribution of the asphalt binders to permanent deformations. $G^*/\sin\delta$ value should be larger than 1000 Pa @ 10 rad/s for the original binder. Higher values of the parameter ratio are expected to result in a higher resistance to permanent deformation. Isochronal plots of $G^*/\sin\delta$ (Figure 4) reveal distinct differences due to the modifiers ability to mix with asphalt. Both of the modified asphalts are qualified according to SHRP specification of the stiffness parameter at 64°C . However, only the blends containing chlorinated HDPE meet the SHRP specification at 70°C . Introduction of chlorine atoms enhances compatibility between the polymer additives and asphalt, thus the volume of the polymer rich phase is increased due to an improved 'solubility' in the asphalt. The increases are significant and are expected to result in improving pavement resistance to rutting when the pavement is open for service.

In order to evaluate the permanent deformation (rutting) and the fatigue cracking of aged asphalt binders, the SHRP specifications require determination of G^* and its components for TFOT and PAV aged materials. The permanent deformation is related to the ratio $G^*/\sin\delta$, which must be at least 2.2 KPa after TFOT aging at the specified high temperature. The product of $G^*\sin\delta$ (or G'') is represented as fatigue cracking factor in asphalt pavements, i.e. a maximum limit of 5000 KPa at a low temperature in

the SHRP asphalt specifications. The ability to dissipate or relax the stress is a desirable binder character in resisting fatigue cracking. An inspection of Figure 5 shows that there is no significant difference between tank AC10 and AC10/HDPE in the TFOT stage. Gross phase separation occurs during thin film aging of the AC10/HDPE blend, which reduces the blend properties to those of unmodified asphalt. The $G^*/\sin\delta$ of AC10/CPE blend is somewhat higher than that of the aged tank asphalt; partial phase separation occurred in this blend at high temperature but the polymer is still contributing to the blend properties. All of these binders meet the qualification of SHRP specifications at 64°C. On the other hand, tests on the fatigue cracking for PAV asphalt binders (Figure 6) show that both the loss modulus (G'') of the PAV aged AC/HDPE and of the AC/CPE blends are less than that of the PAV aged tank asphalt at all temperatures. Extrapolation of the data to the temperature at which $G^*\sin\delta$ reaches 5000 kPa illustrates this point. An estimate of the temperature for AC/HDPE or AC/CPE can be obtained from the intercept of the extrapolation which is much lower than that of the aged tank sample. It appears that a drastic reduction in the loss modulus can be attributed to the polymer additive (HDPE or CPE). This improvement should be effective in reducing age hardening and long term temperature cracking.

Preliminary low temperature creep properties of asphalt blends using a bending beam rheometer can be obtained by knowing the creep load applied to the beam and its deflection at several loading times during the test. According to SHRP program, the stiffness $S(t)$ and the creep rate of the binder under load $m = |d \log S(t) / d \log(t)|$ are reported at the specified temperature after a 60 seconds loading, which simulates the stiffness after two hours at a 10°C lower temperature. A SHRP grade temperature should meet the specifications $S(t=60) \leq 300$ MPa and m -value (slope) ≥ 0.3 . The data in Figure 7 indicate that all asphalt binders met the $S(t)$ and m -value performance criteria for the chosen temperature (-12°C).

The creep and recovery measurements provide rheological data which are characteristic to a particular binder under conditions employed. The constant stress creep/recovery test in Figure 8 illustrates a significant difference between the deformation of CPE and HDPE blends. This observation might be an indication of their rutting resistance, i.e., the lower the deformation, the better the binder response to rutting, which is related to the composition of the asphalt binder. The AC10/CPE material showed a much more pronounced resistance to creep than AC/HDPE or pure asphalt at 50°C. Elastic creep recovery of asphalt samples can be observed after the stress is removed. As expected, the AC10/CPE blend exhibited higher creep recovery than HDPE blend due to the presence of the more elastic filler. On the other hand, the pure asphalt sample did not display any recovery and the presence of HDPE in asphalt did not improve any recovery percentage under these conditions. Therefore, it would be expected to have an asphalt binder with a rutting resistance higher than the maximum resistance imparted by the tank asphalt.

ACKNOWLEDGMENTS

This work was supported by a contract from the Louisiana Transportation Research Center. Special appreciation is extended to Harold Paul who served as the contract technical representative and provided helpful and incisive comments and suggestions.

REFERENCES

1. Anderson, D., Kennedy, T.W., Proceedings of the Association of Asphalt Paving Technologists, 1994, Vol 62, 481.
2. Canterino, P.J., Kahle, G.R., J. Appl. Polym. Sci., 1962, 6, 20.
3. Daly, W. H., Negulescu, I. I., Yeh, P.-H., Prep. Symp. Am. Chem. Soc., Div. Fuel Chem., 1998, 43, 1075.
4. (a) Daly, W. H., Qiu, Z.-Y., Negulescu, I. I., Transportation Research Record, 1996, 1535, 54.
(b) Daly, W. H., Qiu (Chiu), Z.-Y., Negulescu, I. I., Transportation Research Record, 1993, 1391, 56.

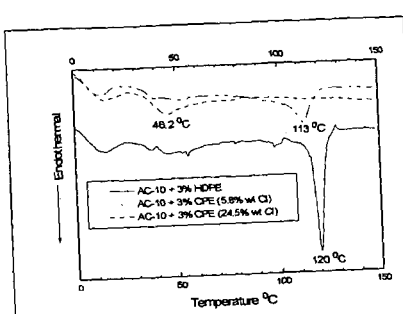


Figure1. DSC thermograms of asphalt AC-10 blended with HDPE or CPE

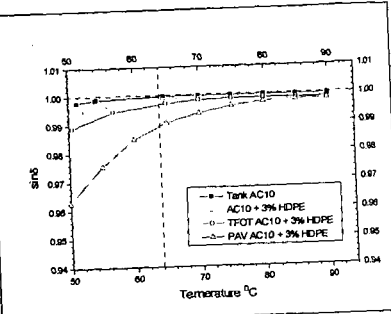


Figure2. Variation of $\sin\delta$ with temperature for a blend of AC-10 with 3% HDPE

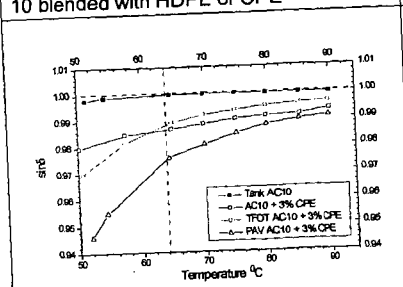


Figure3. Variation of $\sin\delta$ with temperature for a blend of AC-10 with 3% chlorinated HDPE (5.8 wt% Cl)

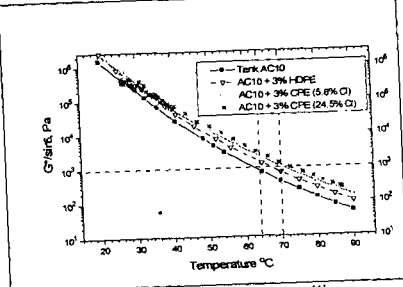


Figure4. Comparison between rutting factors of tank asphalt and blends with HDPE or chlorinated HDPE

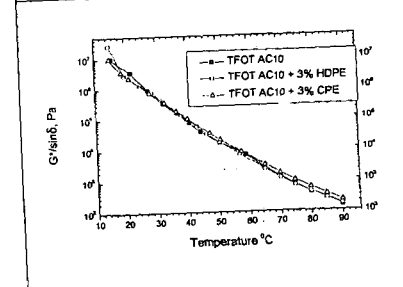


Figure5. Variation of $G^*/\sin\delta$ with temperature for tank asphalt and of blends with HDPE or chlorinated HDPE (5.8 wt% Cl)

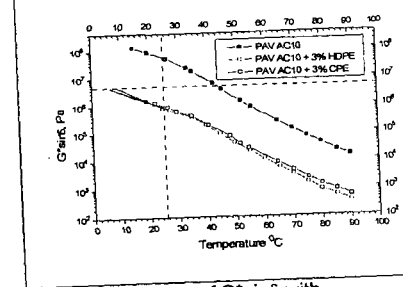


Figure6. Variation of $G^*\sin\delta$ with temperature for tank asphalt and of blends with HDPE or chlorinated HDPE (5.8 wt% Cl)

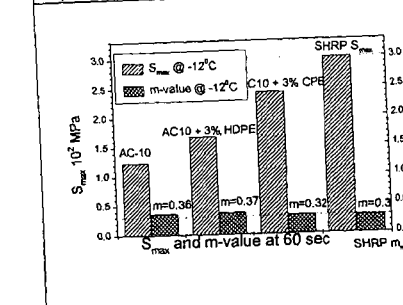


Figure7. Creep stiffness of PAV aged AC10 blends containing HDPE and chlorinated HDPE (5.8 wt% Cl)

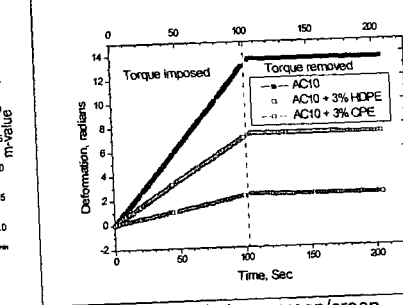


Figure8. Constant stress creep/creep recovery curves at 50 °C of AC10 blends with HDPE or CPE (5.8 wt% Cl)